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AN EXPERIMENTAL INVESTIGATION OF RADIATION EFFECTS IN SEMICONDUCTORS

by W. Dale Compton

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Ву

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INTRODUCTION

Many of the bulk properties of silicon and germanium are drastically altered by irradiation with high energy photons, neutrons, or charged particles. The study of these changes can provide valuable information about the microscopic nature of the defects generated in the solid and the mechanism of defect formation. The present experiments are concerned with the radiation induced changes in the minority carrier lifetime of silicon, of the influence of radiation upon the recombination luminescence of germanium and silicon, and the influence of radiation upon the impurity conduction of germanium. A brief description of the techniques involved and the present status of these studies follows.

CURRENT RESEARCH

RADIATION INDUCED DEFECTS IN SILICON

Electron spin resonance studies of silicon irradiated with fast electrons have been particularly successful in establishing the microscopic models of several prominent defects. In n-type silicon irradiated at room temperature, two prominent defects are found--the Si-A center consisting of a substitutional oxygen atom and the Si-E center consisting of a silicon vacancy trapped next to a substitutional phosphorous atom. The Si-A and Si-E centers are believed to introduce donor levels at about 0.16 eV and 0.40 eV below the edge of the conduction band, respectively. In p-type silicon, the prominent defect appears to be the Si-J center which consists of a divacancy. This center introduces an acceptor level at about 0.27 eV above the top of the valence band.

It should be noted that the observation of defects by electron spin resonance requires that they possess a certain charge configuration. Although the Si-A center cannot be seen by resonance in p-type material, it presumably is formed in much the same concentration as in n-type material. Evidence that this is indeed the case comes from studies of the temperature dependence of minority carrier lifetimes in irradiated p-type silicon. These investigations have observed that the level responsible for recombination is 0.16 eV below the conduction band. The importance of oxygen in the formation of the Si-A center has been amply demonstrated in n-type material. The influence of



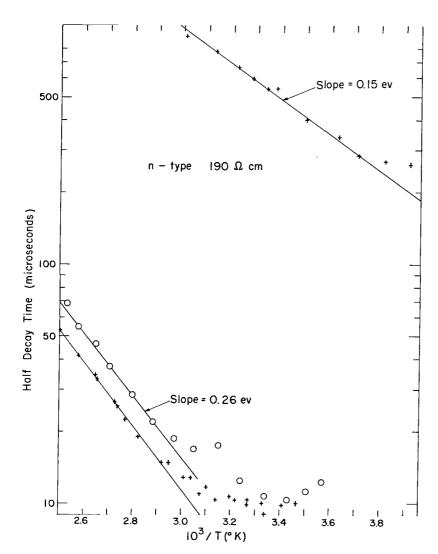


Figure 1. Half decay time of minority carriers \underline{vs} $10^3/T$ for n-type silicon. ρ = 190 ohm-cm at room temperature. Czochralski grown. Upper curve - pre-irradiation. Middle curve - after 1.2 x 10^7 roentgens of Co^{60} . Lower curve - after 1.6 x 10^7 roentgens of Co^{60} .

oxygen upon the recombination level in p-type material has not been well established. Neither has a completely systematic study of the influence of the initial conductivity upon the rate of introduction of Si-A centers been reported nor is the nature of the recombination level in n-type material established.

The present studies are concerned with a systematic investigation of the minority carrier lifetimes in n- and p-type silicon having various initial conductivities. The minority carrier lifetime of each sample will be studied as a function of irradiation dose. Excess carriers are generated by optical injection from a pulsed discharge lamp having a characteristic decay time of about 10-7 sec. An exponential decay of the excess conductivity is observed following the injection of the excess carriers. The time required for the conductivity to decrease to one-half its initial value is plotted as a function of reciprocal absolute temperature. In contrast to previous studies, 3,4 thick samples are being used so that surface recombination processes will be negligible. Irradiation with Co60 gamma

rays is being utilized in order to obtain uniform damage throughout the bulk of the sample.

Figures 1 and 2 present data of the minority carrier lifetimes of n- and p-type silicon, respectively. Figure 1 applies to a sample of n-type 190 ohm-cm material grown by the Czochralski technique. Prior to irradiation, the

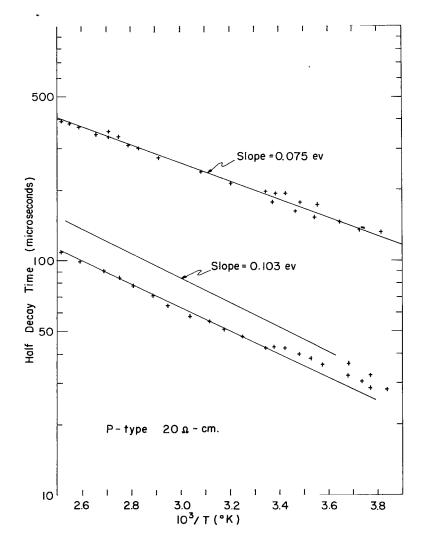


Figure 2. Half decay time of minority carriers $vs = 10^3/T$ for p-type silicon. $\rho = 20$ ohm-cm at room temperature. Floatzone grown. Upper curve - pre-irradiation. Lower curve - after 3.0 x 10^6 roentgens of co^{60} . Middle curve - difference of reciprocal half decay times of upper and lower curves.

recombination level is apparently 0.15 eV above the valence band. Following irradiation with 1.2 and 1.6 x 10^7 roentgens of Co^{60} , the recombination level is located 0.26 eV above the valence band. This compares quite favorably with the location of the level associated with the Si-J center. Although the decrease in lifetime was reasonably linear with the length of irradiation, this will be studied more extensively at a later time. Figure 2 presents data taken on a ptype sample having a room temperature resistivity of 20 ohm-cm. This sample had a low oxygen content as a result of being grown by the floating zone technique. The upper curve was taken on the unirradiated material. The lower curve was obtained after 3 x 10⁶ roentgens of Co⁶⁰ gamma rays. The middle curve is the difference of the reciprocal of the half decay times of the upper and lower curves and represents the effect of the irradiation. The slope of the middle curve is 0.10 eV. irradiation of these samples and additional samples of different initial resistivities and oxygen content is underway.

The recombination of excess minority carriers with majority carriers might be expected to result in the in Fig. 3 for an irradiated

emission of luminescence. This can be depicted as in Fig. 3 for an irradiated p-type sample containing the Si-A center. A free electron and hole are generated by the absorption of a photon. The electron, being the minority carrier, is trapped at the Si-A center. Recombination with one of the many free holes then takes place. For this model, a luminescence with energy of about $\rm E_g$ -0.16 eV should be seen. No recombination luminescence has been reported that results from recombination $\rm via$ radiation induced defects, although recombination

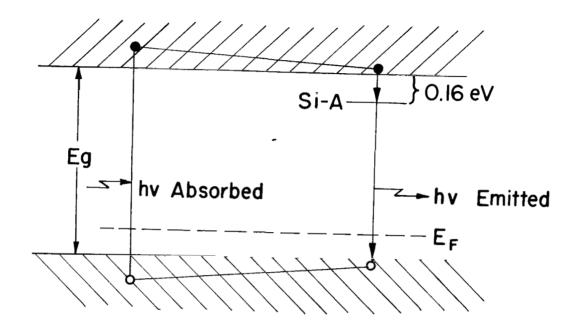


Figure 3. Schematic illustration of absorption and luminescence processes in a semiconductor.

luminescence resulting from recombination \underline{via} donors and acceptor states has been widely studied.⁵ Work is under way to attempt to observe this radiation. If such a luminescence exists, it should provide a very powerful tool for locating the position of the energy levels associated with radiation induced defects.

The equipment for this measurement consists of a monochromator, a cooled PbS detector, a high intensity tungsten light source and chopper. The signal is amplified, transmitted to a synchronous rectifier-amplifier detector and recorded. Since the luminescence characteristic of recombination via induced defects is likely to be very inefficient, the equipment must have a high sensitivity. A reasonable test of this sensitivity would seem to be the observation of the recombination luminescence of silicon and germanium as studied by other workers. An example of this is shown in Fig. 4 for a 20 ohm-cm sample of germanium having a thickness of 0.0069 inches. The sample was etched with CP-4 prior to measurement. These results were obtained at room temperature. An approximate correction for the spectral response of the PbS detector has been made. These data compare very favorably with those published by Haynes. Irradiation of this sample with a flux of 9 x 10¹⁴ nvt fast neutrons resulted in the complete disappearance of this luminescence. No other luminescence could be found at wavelengths less than 2.8 microns.

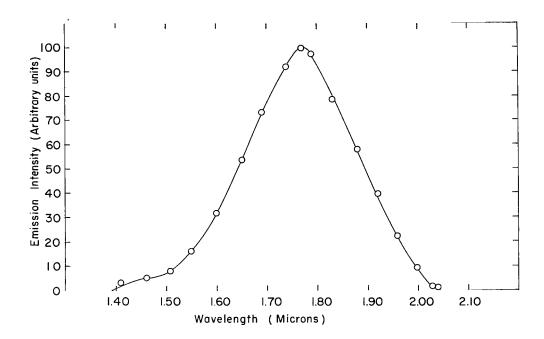


Figure 4. Emission intensity in arbitrary units \underline{vs} wavelength in microns for n-type germanium. $\rho = 20$ ohm-cm at room temperature.

It will be necessary to measure at longer wavelengths with a cooled PbSe detector in order to be certain that no other luminescence is present. Samples of silicon are now being prepared for irradiation and the luminescent spectrum will be studied in the near future.

MECHANISM OF DEFECT PRODUCTION IN GERMANIUM

The search for defects which have been generated by irradiation of germanium with soft x-rays is continuing. The results of these studies may be summarized as follows:

- a. The introduction of acceptor levels into n-type germanium by x-irradiation has an exceedingly small probability.
- b. Although the concentration of conduction electrons changes following irradiation and measurement at quite low temperature, it is difficult to determine whether this results from the introduction of acceptor states or from the trapping of majority carriers--probably at surface states.
- c. If a stable defect involving the donor impurity can be produced by x-irradiation, it would be best to look for such an effect in highly doped material. This requires, however, the detection of a very small change in a large number of conduction electrons.

Because of the above factors, the search for defects produced by x-rays is currently utilizing the study of impurity band conduction. The resistivity and Hall coefficient of samples of n-type germanium containing about 10^{16} donors per $\rm cm^3$ are measured between 80 and 1.5°K. At about 4.5°K the phenomena of impurity conduction occurs. This conduction mechanism may be visualized as follows: The sample contains $\rm N_D$ donor atoms/cm³ and $\rm N_A$ acceptor atoms/cm³. The latter are present as accidental impurities. At absolute zero, the $\rm N_A$ acceptors will contain electrons and $\rm N_D-N_A$ donors will contain electrons. As the temperature is raised, conduction results from the phonon-assisted hopping of electrons from an occupied donor to an unoccupied donor. The resistivity of the sample in this region (T < 4.5°K for $\rm N_D \approx 2 \times 10^{16}/cm^3)$ can be expressed as

$$\rho = \rho_0 e^{-\epsilon_3/kT} \tag{1}$$

where ϵ_3 represents the energy required for an electron to jump from a donor to an unoccupied donor. For low donor concentrations, it has been shown theoretically 6 that ϵ_3 can be expressed as

$$\epsilon_3 = 2 \times 10^{-8} \, (N_D^{1/3} - 1.35 \, N_A^{1/3}) \, \text{eV}$$
 (2)

and that ρ_0 is a constant. Assuming that ρ_0 is independent of N $_D$ and N $_A$, it is straightforward to show that for a constant N $_D$ that $(\triangle \rho/\rho)$ is given by

$$\frac{\triangle \rho}{\rho} \cong -10^{-8} \frac{N_A^{1/3}}{kT} \frac{\Delta N_A}{N_A} . \tag{3}$$

This gives for

$$N_A = 10^{14}/cm^3$$
 and $T = 3^{\circ}K$ $\Delta \rho/\rho \cong -1.6 (\Delta N_A/N_A)$,

and

$$N_A = 10^{16}/cm^3$$
 and $T = 2°K$ $\triangle \rho/\rho \cong -10 (\triangle N_A/N_A)$.

Thus the change in resistivity is a very sensitive detector of the change in the acceptor concentration. As the temperature is raised above that where the impurity band mechanism is important, the free electrons in the conduction band dominate the conduction. If n is the number of free electrons in the conduction band, it can be shown that

$$\frac{n(n + N_A)}{N_D - N_A - n} = 2.0 \times 10^{15} T^{3/2} e^{-\epsilon_d/kT}$$
(4)

where ϵ_d is the activation energy for ionization of a donor electron. Setting

the right hand side of this equation equal to C(T), it can be shown that

$$\frac{\Delta n}{n} = \frac{1 + \frac{C(T)}{n}}{1 + \frac{C(T)}{N_A} + \frac{2n}{N_A}} \frac{\Delta N_A}{N_A}$$
 (5)

for constant N_D . Since the mobility has a temperature dependence that is much less than that of C(T), it follows that

$$\frac{\triangle \rho}{\rho} \approx -\frac{\triangle n}{n}$$
.

For the purpose of comparison, consider the case that $N_A = 0.05 \ N_D$, a physically reasonable choice. The substitution of values into Eq. (5) gives the following:

Table 1. Fractional Change in Carrier Concentration ($\triangle n/n$) as a Function of Temperature and Donor Concentration

.	$N_{\rm D}^{\rm = 2 \times 10^{16}/cm^3}$	$N_A = 1 \times 10^{15} / cm^3$	$N_{\rm D} = 1 \times 10^{14}/{\rm cm}^3$	$N_A = 5 \times 10^{12}/cm^3$
T(°K)	C(T)	∆n/n	C(T)	∆n/n
80 13.3 7.3 5.0	7.67×10^{17} 2.32×10^{15} 4.10×10^{13} 1.01×10^{12}	$0.052 \Delta N_{A}/N_{A}$ $0.11 \Delta N_{A}/N_{A}$ $0.53 \Delta N_{A}/N_{A}$ $1.02 \Delta N_{A}/N_{A}$	3.3×10^{17} 1.7×10^{13} 4.4×10^{9} 2.24×10^{6}	0.053 $\triangle N_A / N_A$ 0.10 $\triangle N_A / N_A$ 1.02 $\triangle N_A / N_A$ 1.06 $\triangle N_A / N_A$

At a given temperature, C(T) is different for the above two examples as a result of the decrease in ϵ_d with increasing donor concentration.

It is quite obvious that the changes of resistivity in the impurity band region are far better indicators of changes in the acceptor concentration than are the changes in the resistivity at higher temperatures. This is particularly true of samples with a high donor concentration. This is illustrated very nicely by the resistivity data of Fig. 5 where impurity conduction is being used as a tool for studying the introduction rate of acceptors by radiation damage. The sensitivity of the impurity conduction process is clearly shown in Fig. 6 where the resistivity data from Fig. 5 are plotted as a function of

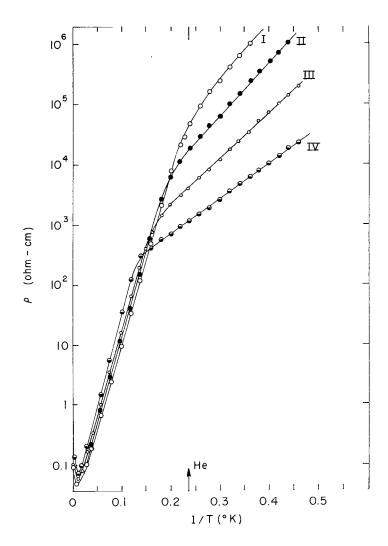


Figure 5. Resistivity vs $1/T(^{\circ}K)$ for n-type germanium containing 1.8 x 10^{16} donors/cm³ and about 1 x 10^{15} acceptors/cm³. Curve I - unirradiated. Curves II, III, and IV after irradiation with 4.5 x 10^{13} , 2.7 x 10^{14} and 2.3 x 10^{15} nvt of fast neutrons, respectively, at room temperature.

neutron flux for two measured temperatures. The lower curve (10°K) is well outside the range of impurity conduction.

It also appears that the introduction of acceptors by irradiation offers a means of obtaining data that are needed for a better understanding of the impurity conduction process. of the great difficulties has been the procurement of samples with the same donor concentration but different acceptor concentrations. Introduction of acceptors by irradiation of n-type germanium leaves the donor concentration constant but increases the acceptor concentration. It should therefore be possible to test the validity of the functional dependence of ϵ_3 upon N_A as given in Eq. (2). One of the difficulties of doing this is the determination of N_A and N_D in the sample prior to irradiation. can be done by carefully fitting the shape of the curve of the Hall coefficient vs 1/T(°K) to the curve predicted by Eq. (4) and thereby determining N_D and N_A . This is being done

with the aid of the IBM 7094 computer. Since Eq. (4) is only valid for donor concentrations less than $10^{16}/\text{cm}^3$, it is necessary to use other techniques for higher donor concentrations.

Since the utilization of these techniques for the study of radiation damage is rather new, it is planned to irradiate samples with a variety of particles which have various initial concentrations of $\rm N_{\rm D}$ and $\rm N_{\rm A}$.

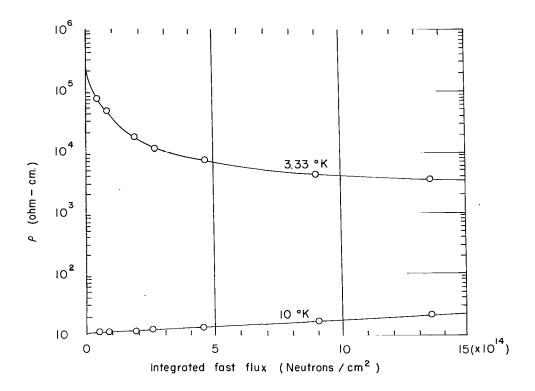


Figure 6. Resistivity vs flux of fast neutrons for sample shown in Fig. 4. Plotted for the measurement temperatures of 3.33 and 10°K.

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277/05

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